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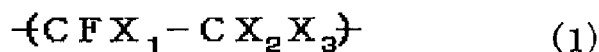
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(54) Title: POLYMER SHEET, METHOD FOR PRODUCING THE SAME, SOLAR BATTERY BACK SHEET USING THE POLYMER SHEET, SOLAR BATTERY MODULE, AND POLYMER DISPERSION LIQUID



(57) Abstract: A polymer sheet according to the present invention includes a polymer layer, and a support, the polymer layer being directly laminated on the support, wherein the polymer layer contains a polymer containing a repeating unit represented by General Formula (1) below, and the amount of the repeating unit represented by General Formula (1) contained in the polymer is 70% by mass or more, General Formula (1) where X₁, X₂ and X₃ each represent any one of a hydrogen atom, a fluorine atom, a chlorine atom and a perfluoroalkyl group having 1 to 3 carbon atoms.



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DESCRIPTION

Title of Invention

POLYMER SHEET, METHOD FOR PRODUCING THE SAME, SOLAR
BATTERY BACK SHEET USING THE POLYMER SHEET, SOLAR
5 BATTERY MODULE, AND POLYMER DISPERSION LIQUID

Technical Field

The present invention relates to a polymer sheet excellent in
water vapor barrier properties, a method for producing the same, a
10 solar battery back sheet using the polymer sheet, a solar battery
module and an aqueous polymer dispersion liquid.

Background Art

Water-vapor-barrier sheets are used for wrapping, solar
15 batteries, and the like. Particularly, amid growing interest in the
problem with global warming from home and abroad, solar batteries
are greatly expected to reduce the emission of carbon dioxides, and
great importance is placed on water-vapor-barrier sheet.

In a solar battery, a solar battery device element (cell) itself is
20 not used alone, several sheets to several tens sheets of solar battery
devices are interconnected in series or in parallel and formed in a
unit. This unit is called "a solar battery module" and typically
composed such that the front surface on which sunlight shines is
covered with a glass face, internally, spaces are filled with a filler
25 made of a thermoplastic material (especially, made of an
ethylene-vinyl acetate copolymer), and the back surface is protected

with a sealing sheet.

Since solar battery modules are primarily used outdoors, they are required to have sufficient durability and weatherability.

Further, back surface sealing sheets are required to have

5 weatherability and a low water vapor permeability. This is because the interconnection is corrosive due to permeation of water, which may adversely affect the output power of the module.

Therefore, a back surface sealing sheet for use in solar batteries needs to be a barrier sheet having very high water vapor
10 barrier properties and weatherability.

As the barrier sheet, there have been various types of barrier sheets known.

For example, an example of a barrier layer produced by vacuum vapor deposition of metal such as aluminum (see PTL 1).

15 However, this method needs a large-size vacuum equipment for production thereof. In addition, since metal deposition layers have conductivity, there is a concern about current leakage when used in solar batteries.

As a barrier layer having no conductivity, there has been also
20 known a method of vacuum depositing a non-metal inorganic material in place of metal (for example, see PTL 2). This method is a method of using a deposition layer of a silicon oxide or an aluminum oxide in place of metal.

Certainly, with this method, a barrier layer having no
25 conductivity can be obtained.

However, with this method, it is liable to cause cracks and film

peel-off attributable to a difference in coefficient of thermal expansion between a support and a deposition layer. In addition, similarly to the case of the above-mentioned metal deposition, this method inconveniently needs to prepare large-size vacuum equipment
5 for producing a barrier sheet.

There have also conventionally known a method of using a barrier layer made of polymer in place of using a non-metal inorganic material (for example, see PTL 3). This method is a method of using a barrier film produced by laminating polyester and a fluorine-based
10 polymer.

However, this method needs an adhesive for laminating the support and the fluorine-based polymer sheet. Adhesive are generally poor in weatherability in comparison with supports and fluorine-based polymer sheets. Therefore, when the solar battery
15 module is used outdoors for a long period of time, it may cause such a disadvantage that a film peel-off occurs between the support and the fluorine-based polymer sheets. Further, this method needs a step of laminating two sheets of films using an adhesive, and thus the production method is complicated.

20 As a method of easily producing a barrier sheet, there have been known a method in which polyvinyl alcohol is applied to a polyester support, followed by drying, rolling, and heating (for example, see PTL 4).

However, a barrier sheet obtained by this method has a
25 problem that the water vapor barrier properties are insufficient, although the oxygen barrier properties are high.

As described above, a technique of a simple method for producing a barrier sheet having sufficient water vapor barrier properties and weatherability has not yet been provided so far, and such a technique has been sought after.

5

Citation List

Patent Literature

- PTL1 Japanese Patent Application Laid-Open (JP-A)
No.10-291569
- 10 PTL2 Japanese Patent Application Laid-Open (JP-A) No.
07-256811
- PTL3 Japanese Patent Application Laid-Open (JP-A) No.
2007-320218
- PTL4 Japanese Patent Application Laid-Open (JP-A) No.
15 2001-293833

Non-Patent Literature

- NPL1 "Polymer Latex" written by Soichi Muroi and Ikuo Morino, published by Kobunshi Kankoukai (1988)
- NPL2 "Chemistry of Polymer Latex" written by Soichi
20 Muroi, published by Kobunshi Kankoukai (1973)
- NPL3 "New Synthetic Resin Emulsion – New Technology
for provision of Functionality and Water Resistance" (*Atarashii
Gousei-Jushi Emulsion - Kinouka To Taisuika No Shin-Gijutsu*)
written by Fumitoshi Tsukiyama, published by Nihon Kagaku Jouho
25 K.K, (2001)
- NPL4 "Surfactant" (*Kaimen Kasseizai Binran*) (compiled

by Ichiro Nishi, Jiichiro Imai, and Masazo Kasai, published by Sangyo Tosho (1960)

Summary of Invention

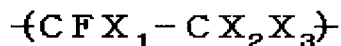
5 Technical Problem

The present invention aims to solve the above-mentioned conventional problems and achieve the following object. That is, an object of the present invention is to provide a polymer sheet which is easily producible and has low water vapor permeability, excellent
10 adhesion properties to a support, and sufficient water vapor barrier properties and weatherability, a method for producing the polymer sheet, a solar battery back sheet, a solar battery module, and an aqueous polymer dispersion liquid each using the polymer sheet.

15 Solution to Problem

Means for solving the above-mentioned problems are as follows:

< 1 > A polymer sheet including:
a polymer layer, and
20 a support,
the polymer layer being directly laminated on the support,
wherein the polymer layer contains a polymer containing a repeating unit represented by General Formula (1) below, and the amount of the repeating unit represented by General Formula (1)
25 contained in the polymer is 70% by mass or more,



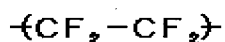
General Formula (1)

where X₁, X₂ and X₃ each represent any one of a hydrogen atom, a fluorine atom, a chlorine atom and a perfluoroalkyl group having 1 to 3 carbon atoms.

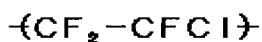
5 < 2 > The polymer sheet according to < 1 > above, wherein the amount of the repeating unit represented by General Formula (1) contained in the polymer is 80% by mass to 97% by mass.

 < 3 > The polymer sheet according to one of < 1 > and < 2 > above, wherein the polymer contained in the polymer layer contains a
10 repeating unit having at least one selected from a carboxyl group, a hydroxyl group and a (meth)acrylamide group in an amount of 0.03% by mass to 20% by mass.

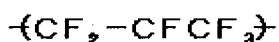
 < 4 > The polymer sheet according to any one of < 1 > to < 3 > above, wherein the repeating unit represented by General Formula
15 (1) is represented by any one of General Formulae (2) to (4) below:



General Formula (2)



General Formula (3)



General Formula (4)

 < 5 > The polymer sheet according to any one of < 1 > to < 4 >
20 above, wherein the degree of crystallization of the polymer contained in the polymer layer is in the range of 30% to 95%.

 < 6 > The polymer sheet according to any one of < 1 > to < 5 >, wherein the polymer layer has a thickness of 1 μm to 20 μm.

< 7 > The polymer sheet according to any one of < 1 > to < 6 > above, wherein the support contains at least one selected from the group consisting of polyester resins, polycarbonate resins, polystyrene resins, acrylic resins and polyimide resins.

< 8 > A solar battery back sheet including:

the polymer sheet according to any one of < 1 > to < 7 > above.

< 9 > A solar battery module including:

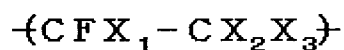
the solar battery back sheet according to < 8 > above.

< 10 > A method for producing a polymer sheet, the method

including:

directly applying an aqueous polymer dispersion onto the support to form a polymer layer,

wherein the aqueous polymer dispersion includes a polymer containing a repeating unit represented by General Formula (1) below, and the amount of the repeating unit represented by General Formula (1) contained in the polymer is 70% by mass or more,



General Formula (1)

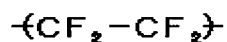
where X_1 , X_2 and X_3 each represent any one of a hydrogen atom, a fluorine atom, a chlorine atom and a perfluoroalkyl group having 1 to 3 carbon atoms.

< 11 > The method for producing a polymer sheet according to < 10 > above, wherein the amount of the repeating unit represented by General Formula (1) contained in the polymer is 80% by mass to 97% by mass.

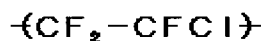
< 12 > The method for producing a polymer sheet according to

one of < 10 > and < 11 > above, wherein the polymer contained in the polymer layer contains a repeating unit having at least one selected from a carboxyl group, a hydroxyl group and a (meth)acrylamide group in an amount of 0.03% by mass to 20% by mass.

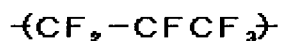
5 < 13 > The method for producing a polymer sheet according to any one of < 10 > to < 12 > above, wherein the repeating unit represented by General Formula (1) is represented by any one of General Formulae (2) to (4) below:



General Formula (2)



10 General Formula (3)



General Formula (4)

< 14 > The method for producing a polymer sheet according to any one of < 10 > to < 13 > above, wherein the polymer layer has a thickness of 1 μm to 20 μm .

15 < 15 > The method for producing a polymer sheet according to any one of < 10 > to < 14 > above, wherein the polymer contained in the aqueous polymer dispersion liquid has a core-shell structure in which each core portion is covered with a shell portion,

 wherein the core portion contains the polymer containing the repeating unit represented by General Formula (1) in an amount of 70% by mass or more and a repeating unit having at least one selected from a carboxyl group, a hydroxyl group and a (meth)acrylamide group in an amount of 0.01% by mass to 30% by mass, and wherein the shell portion contains the polymer containing the repeating unit

represented by General Formula (1) in an amount of 70% by mass or more and the repeating unit having at least one selected from a carboxyl group, a hydroxyl group and a (meth)acrylamide group in an amount of 0.01% by mass to 30% by mass.

5 < 16 > The method for producing a polymer sheet according to < 15 > above, wherein the amount of the repeating unit represented by General Formula (1) contained in the core portion and the shell portion is 80% by mass to 97% by mass.

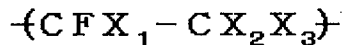
 < 17 > The method for producing a polymer sheet according to
10 any one of < 10 > to < 16 > above, wherein the support contains at least one selected from the group consisting of polyester resins, polycarbonate resins, polystyrene resins, acrylic resins and polyimide resins.

 < 18 > The method for producing a polymer sheet according to
15 any one of < 10 > to < 17 > above, further including heating, at a temperature of 200°C or higher for 5 seconds or longer, the polymer layer which has been formed by applying the aqueous polymer dispersion liquid onto the support.

 < 19 > The method for producing a polymer sheet according to
20 any one of < 15 > to < 18 >, wherein a mass ratio of the shell portion to the core portion is 0.1 to 0.4.

 < 20 > An aqueous polymer dispersion liquid including:
a polymer containing a repeating unit represented by General Formula (1) below,

25 wherein the amount of the repeating unit represented by General Formula (1) contained in the polymer is 70% by mass or more,



General Formula (1)

where X₁, X₂ and X₃ each represent any one of a hydrogen atom, a fluorine atom, a chlorine atom and a perfluoroalkyl group having 1 to 3 carbon atoms.

5

Advantageous Effects of Invention

The present invention can solve the above-mentioned conventional problems and provide a polymer sheet which is easily producible and has low water vapor permeability, excellent adhesion properties to a support, and sufficient water vapor barrier properties and weatherability, a method for producing the polymer sheet, a solar battery back sheet, a solar battery module, and an aqueous polymer dispersion liquid each using the polymer sheet.

15 Brief Description of Drawings

FIG. 1 is an end view illustrating the outline of a polymer sheet according to the present invention.

FIG. 2 is a schematic view illustrating one example of a solar battery device according to the present invention.

20

Description of Embodiments

(Polymer Sheet)

A polymer sheet according to the present invention includes a support and a polymer layer which is directly laminated on the support.

25

- Support -

A material forming the support is not particularly limited and may be suitably selected in accordance with the intended use.

Examples thereof include polyester resins, polycarbonate resins, polystyrene resins, acrylic resins, and polyimide resins. From the viewpoints of cost and mechanical strength, polyester resins and polycarbonate resins are preferable. Among these resins, polyethylene terephthalate and polyethylene naphthalate are particularly preferable. These may be used alone or in combination.

The thickness of the support is not particularly limited and may be suitably selected in accordance with the intended use. It is, however, preferably 30 μm to 400 μm , and more preferably 60 μm to 300 μm .

When the thickness of the support is 30 μm or more, it is advantageous in handleability. When it is 400 μm or less, it is advantageous in costs and the capability of making a solar battery module thin.

The support may be subjected to surface treatment as required.

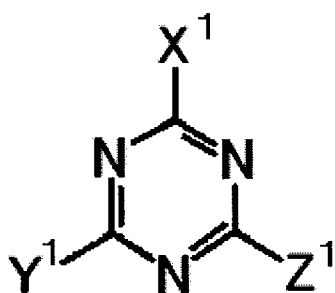
The surface treatment method is not particularly limited and may be suitably selected in accordance with the intended use. For example, a corona treatment, a flame treatment, and a glow discharge treatment are exemplified.

From the viewpoint of light resistance, it is preferable to add a ultraviolet absorber to the support.

The ultraviolet absorber is not particularly limited and may be suitably selected in accordance with the intended use. Examples

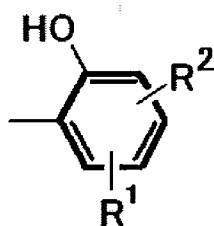
thereof include ultraviolet absorbers having a structure represented by the following General Formula (I), benzophenone-based, benzotriazole-based absorbers, salicylate-based, cyanoacrylate-based, benzoxazine-based, triazine-coumarin copolymer-based ultraviolet
 5 absorbers.

Note that as a conventionally known technique concerning the ultraviolet absorber, all the technical items described in Japanese Patent Application Laid-Open (JP-A) No. 2002-244247 can be used.



General Formula (I)

In General Formula (I), X¹, Y¹ and Z¹ each represent any one of a substituted or unsubstituted alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, and a hetero-ring group; and at least one selected from X¹, Y¹ and Z¹ represents a substituent represented by the following Structural
 10 Formula (A).
 15



Structural Formula (A)

In Structural Formula (A), R¹ and R² each represent any one of a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, an alkenyl group, an aryl group, an alkoxy group, an

acyloxy group, an alkylthio group, an arylthio group, an amino group, an acyl group, an oxycarbonyl group, a carbamoyl group, a sulfamoyl group, a carboxyl group or salt thereof, and a sulfo group or salt thereof. Note that adjacent R¹ and R² may be linked to form a ring.

5 The addition amount of the ultraviolet absorber is preferably controlled so that the support containing the ultraviolet absorber has a light transmittance of light having a wavelength of 380 nm is 3.00% or lower.

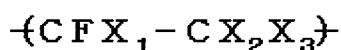
10 To control the light transmittance to 3.00% or lower, the amount of the ultraviolet absorber contained in the support is preferably adjusted in the range of 0.1% by mass to 5.0% by mass, more preferably adjusted in the range of 0.2% by mass to 3.0% by mass, and particularly preferably adjusted in the range of 0.3% by mass 2.0% by mass.

15 - Polymer Layer -

 The polymer layer contains the following polymer.

-- Polymer --

 The polymer is a polymer containing a repeating unit represented by the following General Formula (1).



General Formula (1)

 In General Formula (1), X₁, X₂ and X₃ each represent any one of a hydrogen atom, a fluorine atom, a chlorine atom and a perfluoroalkyl group having 1 to 3 carbon atoms.

 When the polymer containing the repeating unit represented by
25 General Formula (1) is used, a polymer layer provided by using a

coating liquid containing an aqueous dispersion of the polymer can be formed without being peeled off from the support.

The polymer for use in the polymer layer is not particularly limited, as long as it is a polymer containing the repeating unit represented by General Formula (1), and may be suitably selected in accordance with the intended use. It is, however, preferably a polymer represented by at least one selected from the following General Formulae (2) to (4).



As specific examples of the polymer, there are polytetrafluoroethylene (hereinbelow, may be abbreviated as PTFE), polyvinyl fluoride (hereinbelow, may be abbreviated as PVF), polyvinylidene fluoride (hereinbelow, may be abbreviated as PVDF), polyethylene chloride trifluoride (hereinbelow, may be abbreviated as PCTFE), and polytetrafluoro propylene (hereinbelow, may be abbreviated as HFP), for example.

Each of these polymers may be a homopolymer produced by polymerization of a single monomer or a copolymer produced by copolymerization of two or more kinds of monomers having a repeating unit represented by $\text{-(CFX}_1\text{-CX}_2\text{X}_3\text{)-}$. Examples thereof include a copolymer produced by copolymerization of tetrafluoroethylene and tetrafluoropropylene (hereinbelow, may be

abbreviated as P(TFE/HFP)), and a copolymer produced by tetrafluoroethylene and vinylidene fluoride(hereinbelow, may be abbreviated as P(TFE/VDF)).

Further, the polymer may be a polymer produced by
5 copolymerization of a monomer represented by $-(CFX_1-CX_2X_3)-$ and a copolymerizable monomer other than the former monomer.

Examples of the copolymerizable monomer include ethylene, propylene, methyl methacrylate, styrene, and acrylonitrile.

Preferred examples of the copolymer produced by copolymerization of
10 these monomers are a copolymer between tetrafluoroethylene (hereinbelow, may be abbreviated as TFE) and ethylene (hereinbelow, may be abbreviated as P(TFE/E)), a copolymer between tetrafluoroethylene and propylene (hereinbelow, may be abbreviated as P(TFE/P)), a copolymer between chlorotrifluoroethylene
15 (hereinbelow, may be abbreviated as CTFE) and ethylene (hereinbelow, may be abbreviated as P(CTFE/E)), a copolymer between chlorotrifluoroethylene and methyl methacrylate (hereinbelow, may be abbreviated as P(CTFE/MMA)), a copolymer between tetrafluoroethylene and an acrylic acid (hereinbelow, may be
20 abbreviated as P(AA/TFE)), a copolymer between chlorotrifluoroethylene and an acrylic acid (hereinbelow, may be abbreviated as P(AA/CTFE)), a copolymer between hexafluoropropylene and an acrylic acid (hereinbelow, may be abbreviated as P(AA/HFP)), a copolymer between
25 chlorotrifluoroethylene and a methacrylic acid (hereinbelow, may be abbreviated as P(MAA/CTFE)), a copolymer of chlorotrifluoroethylene,

methacrylate and methacrylic acid (hereinbelow, may be abbreviated as P(MAA/MMA/CTFE)), a copolymer of chlorotrifluoroethylene, tetrafluoroethylene and acrylic acid (hereinbelow, may be abbreviated as P(AA/TFE/CTFE)), and a
5 copolymer of ethylene, chlorotrifluoroethylene and acrylic acid (hereinbelow, may be abbreviated as P(AA/CTFE/E)).

Further, as the copolymerizable monomer, there may be exemplified a monomer having a carboxyl group (e.g., acrylic acid and methacrylic acid); a monomer having a hydroxyl group (e.g., hydroxy
10 acrylate and hydroxy methacrylate); and a monomer having a (meth)acrylamide group (e.g., acrylamide and methacrylamide).

The amount of the repeating unit represented by General Formula (1) contained in the polymer contained in the polymer layer is 70% by mass or more, and preferably 80% by mass to 97% by mass.

15 When the amount of the repeating unit is less than 70% by mass, sufficient water vapor barrier properties cannot be obtained, and when the amount is more than 97% by mass, the adhesiveness between the support and the polymer layer may degrade.

The polymer contained in the polymer layer is not particularly
20 limited, however, the polymer preferably contains a repeating unit having at least one selected from a carboxyl group, a hydroxyl group and a (meth)acrylamide group in an amount of 0.03% by mass to 20% by mass, more preferably in an amount of 0.05% by mass to 10% by mass, and particularly preferably in an amount of 0.5% by mass to 5%
25 by mass.

When the amount of the above-mentioned repeating unit is less

than 0.03% by mass, the stability of the aqueous polymer dispersion may be insufficient, and the polymer component may aggregate during storage. When the amount is more than 20% by mass, the water vapor barrier properties may degrade.

5 The polymer for use in the polymer layer is not particularly limited. It is, however, preferably an aqueous polymer dispersion liquid (polymer latex) having a core and a shell of the polymer having the repeating unit represented by $-(CFX_1-CX_2X_3)-$.

As for the aqueous polymer dispersion liquid, for example, the
10 techniques described in NPL 1 ("Polymer Latex" written by Soichi Muroi and Ikuo Morino, published by Kobunshi Kankoukai (1988)); NPL 2 ("Chemistry of Polymer Latex" written by Soichi Muroi, published by Kobunshi Kankoukai (1973)); and NPL 3 ("New Synthetic Resin Emulsion – New Technology for provision of
15 Functionality and Water Resistance" (*Atrashii Gousei-Jushi Emulsion - Kinouka To Taisuika No Shin-Gijutsu*) written by Fumitoshi Tsukiyama, published by Nihon Kagaku Jouho K.K, (2001)) can be used.

The volume average particle diameter of latex particles in the
20 aqueous polymer dispersion liquid is not particularly limited, however, preferably 0.01 μm to 500 μm , and more preferably 0.05 μm to 300 μm .

As the dispersion medium of the aqueous polymer dispersion liquid, water is preferable. However, the dispersion medium may
25 contain a water-miscible organic solvent, such as acetone, methyl alcohol, ethyl acetate, and N-methylpyrrolidone, in an amount of 30%

by mass or less.

The aqueous polymer dispersion liquid may further contain known polymer latex additives as required, such as nonionic, anionic, betaine-based, and cationic surfactants, a viscosity adjustor, an anti-foaming agent, a pH adjustor, and a film-forming auxiliary (which may be called a film-forming aid or a temporally plasticizer). These additives are also described in NPL 1 and NPL 2.

Further, the aqueous polymer dispersion liquid (latex) particles of the present invention is preferably a core-shell latex having internally a core portion, and externally a shell portion having a different composition from the core portion.

The core-shell latex is not particularly limited. For example, the technique described on page 66 in NPL 1 can be used.

The method for synthesizing the core-shell latex is not particularly limited. For example, the core-shell latex can be synthesized by a known emulsion polymerization method. As a specific method therefor, for example, the technique described on page 68 in NPL 1 can be used.

The core portion and the shell portion of the core-shell latex are not particularly limited. However, the core portion and the shell portion are different from each other in polymer structure, and a polymer in which each of the core portion and the shell portion contains a repeating unit represented by General Formula (1).

Specific examples of the polymer include the homopolymers and copolymers described in the section "aqueous polymer dispersion liquid". Especially, from the viewpoints of barrier properties and

adhesiveness to the support, the total amount of monomers having a carboxyl group, a hydroxyl group, and an acrylamide group in the core portion be less than that of the shell portion.

The mass ratio of shell to core (shell/core) in the core-shell latex is preferably 0.1 to 0.4. When the mass ratio is less than 0.1, the adhesiveness may degrade. In contrast, when the mass ratio is more than 0.4, the transmission rate may decrease.

Specifically, the core portion contains the polymer containing the repeating unit represented by General Formula (1) in an amount of 70% by mass or more and the repeating unit having at least one selected from a carboxyl group, a hydroxyl group and a (meth)acrylamide group in an amount of 0.01% by mass to 30% by mass, and the shell portion contains the polymer containing the repeating unit represented by General Formula (1) in an amount of 70% by mass or more and the repeating unit having at least one selected from a carboxyl group, a hydroxyl group and a (meth)acrylamide group in an amount of 0.01% by mass to 30% by mass. Here, the amount of the repeating unit containing at least one selected from a carboxyl group, a hydroxyl group and an acrylamide group contained in the core portion and the shell portion is preferably 0.03% by mass to 20% by mass. Further, the amount of the repeating unit represented by General Formula (1) in the core portion and the shell portion is preferably 80% by mass to 97% by mass.

The degree of crystallization of the polymer layer serving as a binder is not particularly limited, however, it is preferably 30% to 95%.

When the degree of crystallization is lower than 30%, the barrier properties may be insufficient, and when it is higher than 95%, the adhesiveness of the polymer layer to the support may be insufficient. With the degree of crystallization being within 30% to 95%, both the barrier properties and the adhesiveness are excellent, and such a polymer can be favorably used as a back sheet for solar battery.

The specific method of determining the degree of crystallization is as follows.

Only polymer is applied onto a support without using additives, and then subjected to drying and heating treatment in the same manner as used in formation of the polymer layer. A density d of the thus obtained polymer is measured, and a degree of crystallization X_c is calculated using the following Equation (A).

$$X_c = (1/d - 1/\rho_a) / (1/\rho_c - 1/\rho_a) \quad \text{Equation (A)}$$

In Equation (A), ρ_a represents a density of an amorphous portion, and ρ_c represents a density of a crystallized portion.

-- Other Additives --

Further, when necessary, a surfactant, a matting agent, and a lubricant may be added to the polymer layer.

The surfactant is not particularly limited, and known anionic, nonionic and cationic surfactants may be used. For example, those described in NPL 4 ("Surfactant" (*Kaimen Kasseizai Binran*) (compiled by Ichiro Nishi, Jiichiro Imai, and Masazo Kasai, published by Sangyo Tosho (1960)) can be used.

The matting agent is not particularly limited. For example,

fine particles, for example, of silica, titanium oxide, polystyrene, polymethyl methacrylate having a volume average particle diameter of 0.2 μm to 10 μm can be used.

The lubricant is not particularly limited. For example, wax,
5 low-molecular weight polyolefin, silicone, and $\text{C}_n\text{H}_{2n+1}\text{SO}_3\text{Na}$ (n is a natural number of 5 to 15) can be used.

The polymer layer preferably contains no organic solvent. Specifically, the amount of the organic solvent contained in the polymer is preferably less than 0.1% by mass. When the amount of
10 the organic solvent is 0.1% by mass or more, the transmittance of the polymer sheet may decrease.

- Coating Liquid -

The coating liquid is composed of an aqueous medium containing the aqueous dispersion of the polymer (aqueous polymer
15 dispersion) and as necessary, further contains other additives.

-- Aqueous Medium --

The polymer layer is formed by applying an aqueous coating liquid onto the support.

Here, the term "aqueous medium" means a liquid containing
20 water in an amount of 50% by mass or more, in the solvent forming the coating liquid (here, in the case of a dispersion medium, the dispersion medium is also referred to as "solvent").

The aqueous medium is not particularly limited and may be suitably selected in accordance with the intended use. Water may be
25 used singly, and a mixture of water with an organic solvent miscible in water may be used.

The organic solvent is not particularly limited and may be suitably selected in accordance with the intended use. Examples thereof include methanol, ethanol, isopropanol, acetone, and N-methylpyrrolidone.

5 As the aqueous medium in which water is mixed with an organic solvent, there may be exemplified water/methanol = 80/20, water/isopropanol = 75/25, and water/acetone = 90/10 (each of which is represented by a mass ratio).

Note that when the organic solvent is used, it is preferable that
10 the organic solvent be vaporized in a drying step so as not to be incorporated into the polymer layer. When the amount of the organic solvent in the polymer layer is more than 0.1% by mass, the transmittance may decrease. Therefore, it is necessary to determine the maximum addition amount of the organic solvent to the aqueous
15 medium in consideration of this point.

-- Film thickness --

The thickness of the polymer is not particularly limited, however, preferably 1 μm to 20 μm .

The thickness of the polymer is less than 1 μm , necessary water
20 vapor barrier properties may not be obtained, and when the thickness is more than 20 μm , it is disadvantageous in costs.

-- Heat Treatment --

As a method of forming the polymer, after formation of the polymer layer, it is preferably subjected to heat treatment.

25 The heat treatment is not particularly limited. The polymer may be heated at a temperature of 180°C or higher for 5 seconds or

longer, and may be heated at a temperature of 120°C or higher for 3 minutes or longer. The temperature of the heat treatment is not particularly limited, however, it is preferably 200°C to 400°C, and more preferably 250°C to 350°C. When the heat treatment temperature is lower than 120°C, sufficient water vapor barrier properties may not be obtained. When the heat treatment temperature is higher than 400°C, the polymer layer may be thermally degraded.

The heat treatment time is not particularly limited, however, it is preferably 5 seconds to 15 minutes, and more preferably 10 seconds to 3 minutes. When the heat treatment time is shorter than 5 seconds, sufficient water vapor barrier properties may not be obtained. When the heat treatment time is longer than 15 minutes, the polymer layer may be thermally degraded.

The heat treatment method is not particularly limited. For example, known methods, such as a method of blowing hot air, and a method of heating the polymer layer with infrared rays, can be used.

To prevent deterioration of the support in the heat treatment, a method is also preferable in which the support is cooled from the back surface.

- Other Layers -

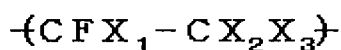
The polymer sheet may be provided with other layers within a range without impairing the effects of the present invention. For example, various layers such as a surface protective layer may be exemplified. The binder, additives, film thickness and coating method for these layers are not particularly limited, and known ones

may be used.

The structure of the polymer sheet of the present invention described above is illustrated in FIG. 1. FIG. 1 illustrates the structure of a polymer sheet 1 of the present invention, in which a polymer layer 3 is provided, in a two-layer structure, on a support 2 without via other layers such as an adhesive layer.

(Method for producing polymer sheet)

A method for producing a polymer sheet of the present invention includes directly applying an aqueous polymer dispersion onto a support to form a polymer layer, wherein the aqueous polymer dispersion contains a polymer containing a repeating unit represented by General Formula (1) below, and the amount of the repeating unit represented by General Formula (1) contained in the polymer is 70% by mass or more. The amount of the repeating unit represented by General Formula (1) contained in the polymer is more preferably 80% by mass to 97% by mass.



General Formula (1)

(In General Formula (1), X_1 , X_2 and X_3 each represent any one of a hydrogen atom, a fluorine atom, a chlorine atom and a perfluoroalkyl group having 1 to 3 carbon atoms.)

The polymer film is not particularly limited. Examples thereof include polyester resins (especially, polyethylene terephthalate resin or polynaphthalate resin), polycarbonate resins, polystyrene resins, acrylic resins, and polyimide resins.

Concerning matters other than this point, matters described

for the polymer sheet of the present invention can be employed.

(Solar Battery Back Sheet and Solar Battery Module)

The polymer sheet can be used for wrapping films, wrapping sheets and the like, and more suitably used as a solar battery back sheet and used in a solar battery module provided with the solar battery back sheet.

- Solar battery Back Sheet -

The solar battery back sheet includes the polymer sheet of the present invention.

- Solar Battery Module -

The solar battery module is provided with the solar battery back sheet.

Other configurations of the solar battery module are not particularly limited, as long as they may be configured so as not to impair the effects of the present invention, and may be suitably selected in accordance with the intended use.

FIG. 2 is a schematic view illustrating one example of a solar battery module 10 according to the present invention.

In FIG. 2, reference numeral 11 denotes glass, reference numeral 12 denotes a filler, reference numeral 13 denotes a solar battery back sheet according to the present invention, reference numeral 14 denotes solar batteries (cells), reference numeral 15 denotes frames, reference numeral 16 denotes a sealant, and reference numeral 17 denotes an interconnection.

In the solar battery device (module) 10 in FIG. 2, light is emitted from the side of the glass 11.

Next, a method for producing a solar battery module according to the present invention will be described with reference to FIG. 2.

(1) The filler 12 is laminated on the (clean) glass 11, and the solar battery cells 14 are arranged on the filler 12.

5 (2) The solar battery back sheet 13 of the present invention is stacked thereon, and heated in this state for about 1 hour so that a layer of the filler 12 is crosslinked.

(3) Any excess in length of the filler 12 and the solar battery back sheet 13 is cut off along the ends of the glass 11.

10 (4) The thus prepared member is pushed into the frames 15 from the side of the glass 11 (which will be a front surface onto which sunlight is incident).

(5) A part of the filler 12 and the solar battery back sheet 13 of the present invention is cut off and the interconnection 17 is soldered to
15 terminal portions of the solar battery cells 14 (the solar battery module 10)

(6) A silicone resin or silicone rubber is applied to the cut portion to seal the terminal portions.

(7) When necessary, a terminal box is provided to perform
20 interconnection.

Note that in FIG. 2, reference numeral 18 denotes an adhesive layer.

Since the solar battery back sheet is used in the solar battery module of the present invention, the solar battery module is excellent
25 in water vapor barrier properties and durability and is easily produced.

Examples

(Synthesis Example)

- Synthesis Example 1: Synthesis of PTFE Latex L-1 -

5 Into a 6 L-stainless steel autoclave equipped with a stirrer,
3,000 mL of deionized water was poured, the following emulsifier was
added thereto so that the concentration reached 600 ppm, and then
ammonium persulfate (APS) serving as an initiator was added thereto
so that the concentration reached 20 ppm. After the atmosphere
10 inside autoclave was sufficiently substituted with nitrogen gas, TFE
was press-fitted until the inside of the autoclave was 0.78 MPa. The
components in the autoclave were heated to 70°C to initiate
polymerization. In accordance with the proceeding of
polymerization, the pressure inside the polymerization system was
15 reduced, and thus TFE was additionally press-fitted to maintain the
pressure inside the autoclave at 0.78 MPa. 18 hours later from the
beginning of the polymerization, TFE was discharged, and then the
temperature of the reaction system was decreased to 25°C to stop the
polymerization reaction. The resulting reaction product was filtered
20 through a 400-mesh filter cloth. Through the above process, PTFE
Latex (L-1) was obtained.

Emulsifier: $\text{CF}_3\text{CF}_2\text{CF}_2\text{C}(\text{CF}_3)_2\text{CH}_2\text{CH}_2\text{COONH}_4$

The solid content concentration and the volume average
particle diameter of the thus obtained latex were measured according
25 to the following methods. PTFE Latex (L-1) was found to have a
solid content concentration of 19.6% by mass and a volume average

particle diameter of 240 nm.

- Measurement method of solid content concentration -

As a latex sample, the latex (about 10 g) was placed on an aluminum pan and heated at 105°C for 2 hours. Based on a ratio of the mass of the heated latex sample and the mass of the latex sample before heated, a solid content concentration thereof was determined.

- Method of measuring volume average particle diameter -

The volume average particle diameter of latex particles was measured using a laser diffraction/scattering type particle size distribution measurement device, LA-950 (manufactured by Horiba Ltd.).

- Synthesis Example 2: Synthesis of PCTFE Latex L-2 -

PCTFE Latex (L-2) was synthesized in the same manner as in Synthesis Example 1, except that the monomer used was changed to CTFE. The thus obtained latex was found to have a solid content concentration of 19.1% by mass and a volume average particle diameter of 250 nm.

- Synthesis Example 3: Synthesis of P(TFE/HFP) Latex L-3 -

P(TFE/HFP) Latex (L-3) was synthesized in the same manner as in Synthesis Example 1, except that the monomer used was changed to TFE/HFP (TFE/HFP = 78/22 (molar ratio)). The thus obtained latex was found to have a solid content concentration of 20.8% by mass and a volume average particle diameter of 260 nm.

- Synthesis Example 4: Synthesis of P(TFE/E) Latex L-4 -

P(TFE/E) Latex (L-4) was synthesized in the same manner as in Synthesis Example 1, except that the monomer used was changed to

TFE/Ethylene (TFE/Ethylene = 90/10 (molar ratio)). The thus obtained latex was found to have a solid content concentration of 19.2% by mass and a volume average particle diameter of 250 nm. (Example 1)

5 - Preparation of PET Support -

Pellets of a polyethylene terephthalate (hereinbelow, abbreviated as PET) resin (intrinsic viscosity = 0.66), which was produced by polycondensation using antimony trioxide as a catalyst, were dried so as to have a water content of 50 ppm or less.

10 Separately, an ultraviolet absorber A (CYASORB UV-3638, produced by Cytec Industries Inc.) (12% by mass) was blended with the resin to prepare masterbatch pellets. The masterbatch pellets were dried so as to have a water content of 50 ppm or less.

Two kinds of these pellets were mixed with each other and
15 melted in an extruder with the temperature of a heater being set from 280°C to 300°C. The blend ratio was controlled so that the amount of the ultraviolet absorber A was 0.7% by mass relative to the total mass of a completed support.

Next the melted PET resin was discharged from a die section
20 onto a chill roll to which electrostatic charged was applied to thereby obtain an amorphous film. Subsequently, the amorphous film was stretched 3.3 times in the longitudinal direction of the film and then stretched 3.8 times in the width direction of the film to thereby produce a biaxially stretched support having a thickness of 100 µm.

25 The support formed of polyethylene terephthalate was subjected to, at its one surface, a corona treatment under the

following conditions. Then, a polymer layer coating liquid having the following composition was applied to the one surface of the support so that a wet coating amount was 34.5 cc/m², followed by drying at 180°C for 5 minutes, thereby obtaining Support 1.

5 - Corona Treatment -

Support 1 was subjected to, at its one surface, a corona treatment while being conveyed at a conveyance speed of 70 m/min under the treatment condition of 730 J/m².

- Preparation of Coating Liquid -

10 Into a 2L-stainless steel vessel equipped with a stirrer, components having the following composition containing Latex (L-1) for use as a binder of a polymer layer were added so that the total amount thereof was 100% by mass, followed by a dispersion treatment, thereby preparing a coating liquid.

15	Latex (L-1)	15% by mass (solid content)
	Surfactant 1	0.005% by mass (solid content)
	Surfactant 2	0.005% by mass (solid content)
	distilled water	Balance

Note that as Surfactants 1 and 2, the following ones were used.

20 Surfactant 1: SANDET BL, solid content 45% by mass, produced by Sanyo Chemical Industries Ltd.

Surfactant 2: NAROAKTY HN-100, produced by Sanyo Chemical Industries Ltd.

- Coating -

25 Subsequently, the support was wet-coated with the coating liquid by a bar coating method.

- Heat Treatment -

The sample was heated by an infrared heater (IDK radiant heater RAK-Model, manufactured by Ishihara Heater K.K.) in a state where the back surface (the opposite surface to the surface provided with the polymer layer) of the sample was closely contacted with a cooling roll with the surface temperature being set to 70°C so that the surface temperature became 330°C. The heat treatment was performed in this state for 3 minutes to thereby obtain a polymer sheet according to Example 1.

The amount of methylethylketone, methyl alcohol, ethyl alcohol, isopropyl alcohol, ethyl acetate, acetone and toluene of the thusly obtained polymer sheet was measured by gas chromatography (Gas Chromatography GC-2010, manufactured by Shimadzu Corporation), however, none of them was detected.

(Examples 2 to 4, Comparative Examples 1 and 2)

Polymer sheets according to Examples 2, 3 and 4 were obtained in the same manner as in Example 1, except that the binder of the polymer sheet was changed from PTFE Latex L-1 synthesized in Synthesis Example 1 to PCTFE Latex L-2, P(TFE/HFP) Latex L-3, and P(TFE/E) Latex L-4 each synthesized in Synthesis Examples 2, 3 and 4, as shown in the following Table 1A, and the conditions for heat treatment were each changed to those shown in the following Table 1A.

Further, polymer sheets according to Comparative Examples 1 and 2 were obtained in the same manner as in Example 1, except that the binder of the polymer sheet was changed from PTFE Latex L-1

synthesized in Synthesis Example 1 to NIPOL Lx811 (acrylic resin, produced by Zeon Corporation), and NIPOL Lx303 (styrene resin, produced by Zeon Corporation) as shown in the following Table 1A, and the conditions for heat treatment were each changed to those shown in the following Table 1A.

(Examples 5 to 9)

Polymer sheets according to Examples 5 to 9 were obtained in the same manner as in Example 2, except that the support was changed to each of them shown in the following Table 1A.

Note that in the following Table 1B, "polyethylene terephthalate (TEONEX Q81)" is a film produced by TEIJIN DUPONT FILMS JAPAN LTD.; "Polycarbonate" is a polycarbonate support produced from TAFLON A2200 (product of Idemitsu Kosan Co., Ltd.); "Polystyrene" is a polystyrene support produced from polystyrene "G690N" (product of Nippon Polystyrene Industry Co., Ltd.); "Polymethylmethacrylate" is a polymethylmethacrylate support produced from polymethylmethacrylate "ACRYPET VH" (product of Mitsubishi Rayon Co., Ltd.); and "Polyimide resin (KAPTON V500)" is a film produced by Dupont-Toray Co., Ltd.

(Examples 10 to 15)

Polymer sheets according to Examples 10 to 15 were obtained in the same manner as in Example 2, except that the wet-coat amount (thickness (μm)) was changed so as to have each polymer layer having the thickness shown in the following Table 1B.

(Examples 16 to 21)

Polymer sheets according to Examples 16 to 21 were obtained

in the same manner as in Example 2, except that the conditions for heat treatment were each changed to those shown in the following Table 1B.

(Comparative Example 3)

5 A PCTFE sheet having a thickness of 4 mm was bonded on the support of Example 1 with the following polyurethane-based adhesive to form a laminate.

 The adhesive was applied so as to have a dry thickness of 150 μm , and after the PCTFE sheet was bonded together with the support,
10 the laminate was heated at 120°C for 30 minutes.

 Note that the support and the PCTFE sheet were preliminarily subjected to, at the contact surface thereof, a corona discharge treatment under the condition of 730 J/m².

• Polyurethane-based adhesive

15 In the polyurethane-based adhesive, to a main agent made of polyester polyol containing a dimer fatty acid, a curing agent made of a bullet form of hexamethylene diisocyanate was added so that the mass ratio is 10:1.

(Measurement/Evaluation Method)

20 - Measurement of Thickness -

 The thickness of the support only was measured by a film thickness meter (DG-525, manufactured by Ono Measurement Equipment). After each polymer layer was provided to the support, the thickness of the formed laminate at the same place was measured
25 similarly. The thickness of only the support was subtracted from the resulting thickness of the laminate to determine the thickness of the

polymer layer.

- Measurement of Coefficient of Moisture Permeability -

After a moisture permeation cup (diameter of sample: 60 mm) was charged with about 1 g of calcium chloride, the sample was set in the moisture permeation cup, and the circumference of the sample was sealed with a wood alloy. Next, the cup was left under an atmosphere controlled to 25°C/60%RH for 2 hours, and then a mass w_1 thereof was measure. Subsequently, the cup was stored under an atmosphere of 25°C/90%RH for 60 days. Thereafter, the cup was left under an atmosphere controlled to 25°C/60%RH for 2 hours, and then a mass w_2 thereof was measure.

From the values of w_1 and w_2 , the coefficient of moisture permeability ($\text{g/m}^2 \cdot \text{day}$) of the sample was calculated by the following Equation 1:

$$(w_2 - w_1) \times \frac{100 \times 100}{3 \times 3 \times 3.14} \times \frac{1}{60} \quad \text{Equation 1}$$

Note that concerning Comparative Examples 1 and 2, the storage period of the polymer sheets at the atmosphere of 25°C/90%RH was changed to 1 day, and then the coefficients of moisture permeability of them were determined using the following Equation 2 instead of Equation 2 described above.

$$(w_2 - w_1) \times \frac{100 \times 100}{3 \times 3 \times 3.14} \quad \text{Equation 2}$$

- Evaluation of Weatherability -

Each polymer sheet was cut into a size of 10 cm × 10 cm and stored at an atmosphere of 85°C/85%RH for 1,000 hours, and then

visually observed for peel-off between the support and the polymer layer. A polymer sheet with no change in appearance is practically usable, and a polymer sheet with any change in appearance is not practically usable.

Table 1A

	Support		Polymer layer				Heat treatment	Evaluation results	
	Type	Thickness (μm)	Type of polymer	Material	Content rate of repeating unit represented by General Formula (1)	Thickness (μm)		Moisture permeability	Weatherability
Ex. 1	Polyethylene terephthalate	100	L-1	PTFE	100%	4.9	330°C 3 min	0.46	Not changed
Ex. 2	Polyethylene terephthalate	100	L-2	PCTFE	100%	5.0	230°C 3 min	0.26	Not changed
Ex. 3	Polyethylene terephthalate	100	L-3	P(TFE/HFP)	100%	4.9	270°C 3 min	0.62	Not changed
Ex. 4	Polyethylene terephthalate	100	L-4	P(TFP/E)	100%	4.8	330°C 3 min	0.68	Not changed
Comp. Ex. 1	Polyethylene terephthalate	100	NIPOL Lx811	Acrylic resin	100%	5.1	230°C 3 min	16.8	Pealed off
Comp. Ex. 2	Polyethylene terephthalate	100	NIPOL Lx303	Styrene resin	100%	5.0	230°C 3 min	11.5	Pealed off
Ex. 5	Polyethylene naphthalate (TEONEX Q81)	125	L-2	PCTFE	100%	4.9	230°C 3 min	0.26	Not changed
Ex. 6	Polycarbonate	125	L-2	PCTFE	100%	4.9	230°C 3 min	0.27	Not changed
Ex. 7	Polystyrene	65	L-2	PCTFE	100%	4.9	230°C 3 min	0.26	Not changed
Ex. 8	Polymethyl methacrylate	65	L-2	PCTFE	100%	4.9	230°C 3 min	0.28	Not changed
Ex. 9	Polyimide resin (KAPTON V500)	125	L-2	PCTFE	100%	4.9	230°C 3 min	0.26	Not changed

Table 1B

	Support		Polymer layer				Heat treatment	Evaluation results	
	Type	Thickness (μm)	Type of polymer	Material	Content rate of repeating unit represented by General Formula (1)	Thickness (μm)		Moisture permeability	Weatherability
Ex. 10	Polyethylene terephthalate	100	L-2	PCTFE	100%	10.1	230°C 3 min	0.13	Not changed
Ex. 11	Polyethylene terephthalate	100	L-2	PCTFE	100%	7.7	230°C 3 min	0.18	Not changed
Ex. 12	Polyethylene terephthalate	100	L-2	PCTFE	100%	3.2	230°C 3 min	0.44	Not changed
Ex. 13	Polyethylene terephthalate	100	L-2	PCTFE	100%	2.4	230°C 3 min	0.58	Not changed
Ex. 14	Polyethylene terephthalate	100	L-2	PCTFE	100%	1.3	230°C 3 min	0.99	Not changed
Ex. 15	Polyethylene terephthalate	100	L-2	PCTFE	100%	0.6	230°C 3 min	2.3	Not changed
Ex. 16	Polyethylene terephthalate	100	L-2	PCTFE	100%	5.0	Not heated	1.28	Not changed
Ex. 17	Polyethylene terephthalate	100	L-2	PCTFE	100%	5.0	120°C 3 min	0.58	Not changed
Ex. 18	Polyethylene terephthalate	100	L-2	PCTFE	100%	5.0	180°C 3 min	0.39	Not changed
Ex. 19	Polyethylene terephthalate	100	L-2	PCTFE	100%	5.0	230°C 10 sec	0.38	Not changed
Ex. 20	Polyethylene terephthalate	100	L-2	PCTFE	100%	5.0	230°C 1 min	0.34	Not changed
Ex. 21	Polyethylene terephthalate	100	L-2	PCTFE	100%	5.0	230°C 10 min	0.25	Not changed
Comp. Ex. 3	Produced by bonding (lamination)							0.46	Peeled off

- Synthesis Example 5: Synthesis of PCTFE Latex L-5 -

Into a 6,000 mL-stainless steel autoclave equipped with a stirrer, 3,000 mL of deionized water was poured, 12 g of the emulsifier ($\text{CF}_3\text{CF}_2\text{CF}_2\text{C}(\text{CF}_3)_2\text{CH}_2\text{CH}_2\text{COONH}_4$) same as that used in Synthesis Example 1 was added thereto, and then 1.2 g of ammonium persulfate (APS) serving as an initiator was added. After the atmosphere inside autoclave was sufficiently substituted with nitrogen gas, CTFE was press-fitted until the inside of the autoclave was 0.8 MPa. The components in the autoclave were heated to 70°C to initiate polymerization. In accordance with the proceeding of polymerization, the pressure inside the polymerization system was reduced, and thus CTFE was additionally press-fitted to maintain the pressure inside the autoclave at 0.8 MPa. The system was polymerized for 20 hours in this state.

Thereafter, the pressure of the reaction system was restored to 1 atmospheric pressure, and the temperature thereof was decreased to 25°C to stop the polymerization reaction.

The pH of the resulting reaction product was controlled to pH 9 with NH_4OH and filtered through a 400-mesh filter cloth.

Through the above process, PCTFE Latex L-5 was obtained.

This latex was found to have a solid content concentration of 26.2% by mass and a volume average particle diameter of 223 nm.

- Synthesis Example 6: Synthesis of P(AA/TFE/CTFE) Latex L-6 -

P(AA/TFE/CTFE) Latex L-6 according to Synthesis Example 6 was obtained in the same manner as in same manner as in Synthesis Example 5, except that instead of additionally press-fitting CTFE to

maintain the inside of the autoclave at 0.8 MPa and performing polymerization for 20 hours in this state, TFE was additionally press-fitted to maintain the pressure inside the autoclave at 0.8 MPa, while adding 72 g of AA dropwise over 24 hours, and the reaction system was polymerized for 24 hours in this state.

This latex was found to have a solid content concentration of 21.7% by mass and a volume average particle diameter of 223 nm.

Synthesis Example 7: Synthesis of Core-Shell Latex L-11

Core-Shell (L-11) was synthesized by performing the following two steps:

(1) Step 1 (Synthesis of Core)

Into a 6,000 mL-stainless steel autoclave equipped with a stirrer, 3,000 mL of deionized water was poured, 12 g of the emulsifier ($\text{CF}_3\text{CF}_2\text{CF}_2\text{C}(\text{CF}_3)_2\text{CH}_2\text{CH}_2\text{COONH}_4$) same as that used in Synthesis Example 1 was added thereto, and then 1.2 g of ammonium persulfate (APS) serving as an initiator was added. After the atmosphere inside autoclave was sufficiently substituted with nitrogen gas, TFE was press-fitted until the inside of the autoclave was 0.8 MPa. The components in the autoclave were heated to 70°C to initiate polymerization. In accordance with the proceeding of polymerization, the pressure inside the polymerization system was reduced, and thus TFE was additionally press-fitted to maintain the pressure inside the autoclave at 0.8 MPa. The polymerization was continued for 18 hours in this state to finish Step 1.

(2) Step 2 (Synthesis of Shell)

Upon completion of Step 1, 15 g of an acrylic acid was added

dropwise over 2 hours into the aqueous phase with the pressure thereof being kept at 0.8 MPa.

After the dropping of the acrylic acid was completed, the pressure inside the container was restored to 1 atmospheric pressure.

5 Thereafter, the temperature of the system was maintained at 70°C for 30 minutes, and then reduced to 25°C to finish Step 2.

Then, the pH of the resulting reaction product was controlled to pH 9 with NH₄OH and filtered through a 400-mesh filter cloth. Through the above process, Core-Shell Latex L-11 was obtained.

10 This latex was found to have a solid content concentration of 24.4% by mass and a volume average particle diameter of 218 nm.

Note that the latex after completion of Step 1 had a solid content concentration of 19.6% and a volume average particle diameter of 202 nm.

15 Further, a core/shell ratio of this latex was measured according to the method described below and found to be 0.24.

- Measurement method of Shell/Core Ratio -

A solid content concentration of a latex sample after completion of (synthesis) Step 1 and after completion of (synthesis) Step 2 was
20 determined. From a solid content concentration C1 measured after completion of the synthesis Step 1 and a solid content concentration C2 measured after completion of the synthesis Step 2, the shell/core ratio of the latex sample was determined by the following equation.

$$\text{Shell/Core Ratio} = C1/(C2 - C1)$$

25 The calculated value results in a value between 0 (zero) and ∞ , zero represents that there is no shell in the latex sample, and ∞

represent that no core is present and the latex sample consists of shells.

- Synthesis Examples 8 and 9: Synthesis of Core-Shell Latexes L-12 and L-13 -

5 Core-Shell Latexes L-12 and L13 according to Synthesis Examples 8 and 9 were obtained in the same manner as in Synthesis Example 7, except that the monomer for use in Steps 1 and 2 was changed from TFE to CTFE and HFP, respectively, as shown in the following Tables 2A to 2D.

10 - Synthesis Example 10: Synthesis of Core-Shell Latex L-14 -

 Core-Shell Latex L-14 according to Synthesis Example 10 was obtained in the same manner as in Synthesis Example 8, except that the monomer for use in Step 1 was changed to CTFE/E in which the molar ratio thereof was adjusted to CTFE/E = 9/1 by controlling the
15 pressure ratio in the polymerization.

- Synthesis Example 11 and 12: Synthesis of Core-Shell Latexes L-15 and L-16 -

 Core-Shell Latexes L-15 and L16 according to Synthesis Examples 11 and 12 were obtained in the same manner as in
20 Synthesis Example 8, except that the monomer for use in Step 2 was changed from CTFE to MAA/MMA in which the mass ratio of MAA/MMA was adjusted to 3/2 by adding a mixture of MAA (10 g) and MMA (5 g) dropwise into the system, as shown in Tables 2A to 2D.

- Synthesis Example 13: Synthesis of Core-Shell Latex L-17 -

25 (1) Step 1 (Synthesis of Core)

 Synthesis of core was performed in the sample manner as in

Step 1 in Synthesis Example 8, except that the polymerization time was changed from 18 hours to 14 hours.

(2) Step 2 (Synthesis of Shell)

Synthesis of core was performed in the same manner as in Step 2 in Synthesis Example 8, except that instead of adding 15 g of the acrylic acid dropwise into the system over 2 hours, 30 g of the acrylic acid was added dropwise into the system over 4 hours, and Core-Shell Latex L-17 according to Synthesis Example 13 was obtained.

This latex was found to have a solid content concentration of 23.9% by mass and a volume average particle diameter of 216 nm.

Note that the latex after completion of Step 1 had a solid content concentration of 15.8% and a volume average particle diameter of 189 nm.

- Synthesis Example 14: Synthesis of Core-Shell Latex L-18 -

(1) Step 1 (Synthesis of Core)

Synthesis of core was performed in the same manner as in Step 1 in Synthesis Example 8, except that the polymerization time was changed from 18 hours to 22 hours.

(2) Step 2 (Synthesis of Shell)

Synthesis of core was performed in the same manner as in Step 2 in Synthesis Example 8, except that instead of adding 15 g of the acrylic acid dropwise into the system over 2 hours, 7.5 g of the acrylic acid was added dropwise into the system over 1 hour, and Core-Shell Latex L-18 according to Synthesis Example 14 was obtained.

This latex was found to have a solid content concentration of 26.6% by mass and a volume average particle diameter of 224 nm.

Note that the latex after completion of Step 1 had a solid content concentration of 24.0% and a volume average particle diameter of 216 nm.

(Examples 22 to 47)

5 Polymer sheets according to Examples 22 to 47 were obtained in the same manner as in Example 1, except that the binder of the polymer layer was changed from PTFE Latex L-1 synthesized in Synthesis Example 1 to PCTFE Latex L-5, P(AA/TFE/CTFE) Latex L-6, and Core-Shell Latexes L-11 to L-18 each synthesized in
10 Synthesis Examples 5 to 14 as shown in the following Tables 2A to 2D, the support was changed to each support shown in Tables 2A to 2D, and the wet coat amount (thickness (μm) of the coating liquid was changed so as to change the thickness of each polymer layer to the value shown in Tables 2A to 2D, and the conditions for heat treatment
15 were changed to those shown in Tables 2A to 2D.

Note that in Tables 2A to 2D, “polyethylene terephthalate (E-20)” and “polyethylene terephthalate (X10S)” each serving as a support are films produced by Toray Industries, Inc.; “polyethylene terephthalate (TEONEX Q81)”, “polycarbonate”, “polystyrene”,
20 “polymethyl methacrylate” and “polyimide resin (KAPTON V500)” are identical to those described in Tables 1A and 1B.

The polymer sheets of Examples 22 to 47 were evaluated for the adhesiveness according to the method described below. Further, the polymer sheets of Examples 22 to 47 were measured for degree of
25 crystallization according the method described below. The evaluation results are shown in Tables 2A to 2D.

- Evaluation method of Adhesiveness -

Each sample of the polymer sheets according to Examples 22 to 47 was cut into a size of 10 cm × 10 cm and exposed to an atmosphere of 25°C/60%RH for 24 hours to make it wet. Thereafter, the surface of the sample (the surface of the polymer layer) was scratched using a single edged razor to make six-by-six scratch marks in height and width (25 grids in total). Note that the surface of the polymer layer was scratched so as to scratch reached the support surface.

A Mylar tape of 25 mm in width was affixed onto the sample and peeled off at a peel angle of 180° by hand, and each of the samples was graded by the number of peeled squares. Adhesiveness degrees were graded into the following five ranks depending on the number of peeled grids. Those allowable to use practically are classified to Ranks 5, 4 or 3.

Rank 5: No peel-off occurred.

Rank 4: The number of peeled grids was less than 1.

Rank 3: The number of peeled grids was 1 or more but less than 5.

Rank 2: The number of peeled grids was 5 grids or more but less than 10.

Rank 1: The number of peeled grids was 10 or more.

- Evaluation Method of Degree of Crystallization -

A latex liquid having a solid content of 15% by mass was applied onto the polyester film so as to have a dry film thickness of 6 μm and then dried at 185°C for 5 minutes. Subsequently, the laminate was subjected to a heat treatment same as is Examples 42 to

47.

Next, the coating layer was separated from the support, and a density d of the polymer was measured using a density gradient tube.

Next, a degree of crystallization X_c was calculated based on the
5 following Equation (A).

$$X_c = (1/d - 1/\rho_a)/(1/\rho_c - 1/\rho_a) \quad \text{Equation (A)}$$

In Equation (A), ρ_a represents a density of an amorphous portion, and ρ_c represents a density of a crystalline portion. Here, ρ_a is 2.072, and ρ_c is 2.183.

Table 2A

	Support		Polymer						Heating treatment	Evaluation Result			
	Type	Thickness (μm)	Type of polymer	Core	Shell	Shell / Core ratio	Content rate of repeating unit represented by General Formula (I)	Thickness (μm)		Moisture permeability	Light resistance	Adhesive-ness	Degree of crystallization
Ex. 22	E-20	75	L-5	PCTFE	Not used	-	100%	6.1	330°C 3 min	0.22	Not changed	3	-
Ex. 23	E-20	75	L-6	P(AA/TFE/CTFE)	Not used	-	94%	6.2	330°C 3 min	2.58	Not changed	5	-
Ex. 24	E-20	75	L-11	PTFE	P(AA/TFE)	0.24	99%	6.2	330°C 3 min	0.53	Not changed	5	-
Ex. 25	E-20	75	L-12	PCTFE	P(AA/CTFE)	0.19	99%	6.2	230°C 3 min	0.27	Not changed	5	-
Ex. 26	E-20	75	L-13	PHFP	P(AA/HFP)	0.18	99%	6.0	270°C 3 min	0.38	Not changed	5	-
Ex. 27	E-20	75	L-14	P(CTFE/E)	P(AA/CTFE/E)	0.19	99%	6.1	330°C 3 min	0.39	Not changed	5	-
Ex. 28	E-20	75	L-15	PCTFE	P(MAA/CTFE)	0.20	99%	6.2	330°C 3 min	0.28	Not changed	5	-

Table 2B

	Support		Polymer						Heating treatment	Evaluation Result			
	Type	Thickness (μm)	Type of polymer	Core	Shell	Shell / Core ratio	Content rate of repeating unit represented by General Formula (1)	Thickness (μm)		Moisture permeability	Light resistance	Adhesive-ness	Degree of crystallization
Ex. 29	E-20	75	L-16	PCTFE	P(MAA/MMA/CTFE)	0.20	99%	6.1	330°C 3 min	0.31	Not changed	5	-
Ex. 30	X10S	250	L-12	PCTFE	P(AA/CTFE)	0.19	99%	6.1	330°C 3 min	0.23	Not changed	5	-
Ex. 31	TEO NEX Q81	125	L-12	PCTFE	P(AA/CTFE)	0.19	99%	6.2	230°C 3 min	0.25	Not changed	5	-
Ex. 32	polycarbonate	125	L-12	PCTFE	P(AA/CTFE)	0.19	99%	6.2	230°C 3 min	0.24	Not changed	5	-
Ex. 33	Polystyrene	65	L-12	PCTFE	P(AA/CTFE))	0.19	99%	6.0	230°C 3 min	0.27	Not changed	5	-
Ex. 34	Poly methyl methacrylate	65	L-12	PCTFE	P(AA/CTFE)	0.19	99%	6.2	230°C 3 min	0.26	Not changed	5	-
Ex. 35	KAPTON V500	125	L-12	PCTFE	P(AA/CTFE)	0.19	99%	6.2	230°C 3 min	0.26	Not changed	5	-

Table 2C

	Support		Polymer						Heating treatment	Evaluation Result			
	Type	Thickness (μm)	Type of polymer	Core	Shell	Shell / Core ratio	Content rate of repeating unit represented by General Formula (1)	Thickness (μm)		Moisture permeability	Light resistance	Adhesiveness	Degree of crystallization
Ex. 36	E-20	75	L-17	PCTFE	P(AA/CTFE)	0.48	97%	6.0	330°C 3 min	0.36	Not changed	5	-
Ex. 37	E-20	75	L-18	PCTFE	P(AA/CTFE)	0.08	99.5%	6.1	330°C 3 min	0.21	Not changed	4	-
Ex. 38	E-20	100	L-12	PCTFE	P(AA/CTFE)	0.19	99%	12.2	230°C 3 min	0.22	Not changed	4	-
Ex. 39	E-20	100	L-12	PCTFE	P(AA/CTFE)	0.19	99%	8.9	230°C 3 min	0.24	Not changed	5	-
Ex. 40	E-20	100	L-12	PCTFE	P(AA/CTFE)	0.19	99%	3.2	230°C 3 min	0.30	Not changed	5	-
Ex. 41	E-20	100	L-12	PCTFE	P(AA/CTFE)	0.19	99%	0.6	230°C 3 min	2.50	Not changed	5	-

Table 2D

	Support		Polymer						Heating treatment	Evaluation Result			
	Type	Thickness (μm)	Type of polymer	Core	Shell	Shell / Core ratio	Content rate of repeating unit represented by General Formula (1)	Thickness (μm)		Moisture permeability	Light resistance	Adhesive-ness	Degree of crystallization
Ex. 42	E-20	100	L-12	PCTFE	P(AA/CTFE)	0.19	99%	6.3	Not heated	1.28	Not changed	5	27%
Ex. 43	E-20	100	L-12	PCTFE	P(AA/CTFE)	0.19	99%	6.3	120°C 3 min	0.95	Not changed	5	32%
Ex. 44	E-20	100	L-12	PCTFE	P(AA/CTFE)	0.19	99%	6.2	180°C 3 min	0.39	Not changed	5	48%
Ex. 45	E-20	100	L-12	PCTFE	P(AA/CTFE)	0.19	99%	6.3	230°C 10 sec	0.38	Not changed	5	42%
Ex. 46	E-20	100	L-12	PCTFE	P(AA/CTFE)	0.19	99%	6.3	230°C 1 min	0.34	Not changed	5	56%
Ex. 47	E-20	100	L-12	PCTFE	P(AA/CTFE)	0.19	99%	6.1	230°C 10 min	0.25	Not changed	5	71%

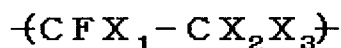
As shown in Tables 1A, 1B, 2A to 2D, the polymer sheets according to the present invention have low water vapor permeability and excellent adhesion to supports. Further, since the polymer sheets have no metal deposition layer and need no lamination using an adhesive, there is no problem with current leakage and their durability when used as a protective sheet of a solar battery. Further, there is no need to use a vacuum in the production process, and thus it is advantageous in costs, because it is unnecessary to prepare vacuum equipment. As described above, the polymer of the present invention is excellent in quality as a barrier film.

Reference Signs List

- | | |
|-------|--------------------------|
| 1 | Polymer sheet |
| 2 | Support |
| 15 3 | Polymer layer |
| 10 | Solar battery module |
| 11 | Glass |
| 12 | Filler |
| 13 | Solar battery back sheet |
| 20 14 | Solar battery cell |
| 15 | Flame |
| 16 | Sealant |
| 17 | Interconnection |
| 18 | Adhesive layer |

CLAIMS

1. A polymer sheet comprising:
a polymer layer, and
a support,
5 the polymer layer being directly laminated on the support,
wherein the polymer layer comprises a polymer containing a
repeating unit represented by General Formula (1) below, and the
amount of the repeating unit represented by General Formula (1)
contained in the polymer is 70% by mass or more,



General Formula (1)

where X_1 , X_2 and X_3 each represent any one of a hydrogen atom,
a fluorine atom, a chlorine atom and a perfluoroalkyl group having 1
to 3 carbon atoms.

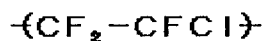
2. The polymer sheet according to claim 1, wherein the amount of
15 the repeating unit represented by General Formula (1) contained in
the polymer is 80% by mass to 97% by mass.

3. The polymer sheet according to one of claims 1 and 2, wherein
the polymer contained in the polymer layer contains a repeating unit
having at least one selected from a carboxyl group, a hydroxyl group
20 and a (meth)acrylamide group in an amount of 0.03% by mass to 20%
by mass.

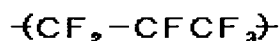
4. The polymer sheet according to any one of claims 1 to 3,
wherein the repeating unit represented by General Formula (1) is
represented by any one of General Formulae (2) to (4) below:



General Formula (2)

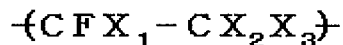


General Formula (3)



General Formula (4)

5. The polymer sheet according to any one of claims 1 to 4,
 5 wherein the degree of crystallization of the polymer contained in the polymer layer is in the range of 30% to 95%.
6. The polymer sheet according to any one of claims 1 to 5,
 wherein the polymer layer has a thickness of 1 μm to 20 μm .
7. The polymer sheet according to any one of claims 1 to 6,
 10 wherein the support contains at least one selected from the group consisting of polyester resins, polycarbonate resins, polystyrene resins, acrylic resins and polyimide resins.
8. A solar battery back sheet comprising:
 the polymer sheet according to any one of claims 1 to 7.
- 15 9. A solar battery module comprising:
 the solar battery back sheet according to claim 8.
10. A method for producing a polymer sheet, the method comprising:
 directly applying an aqueous polymer dispersion onto a support
 20 to form a polymer layer,
 wherein the aqueous polymer dispersion comprises a polymer containing a repeating unit represented by General Formula (1) below, and the amount of the repeating unit represented by General Formula (1) contained in the polymer is 70% by mass or more,



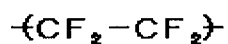
General Formula (1)

where X_1 , X_2 and X_3 each represent any one of a hydrogen atom, a fluorine atom, a chlorine atom and a perfluoroalkyl group having 1 to 3 carbon atoms.

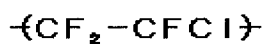
11. The method for producing a polymer sheet according to claim 10, wherein the amount of the repeating unit represented by General Formula (1) contained in the polymer is 80% by mass to 97% by mass.

12. The method for producing a polymer sheet according to one of claims 10 and 11, wherein the polymer contained in the polymer layer contains a repeating unit having at least one selected from a carboxyl group, a hydroxyl group and a (meth)acrylamide group in an amount of 0.03% by mass to 20% by mass.

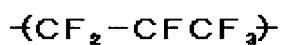
13 The method for producing a polymer sheet according to any one of claims 10 to 12, wherein the repeating unit represented by General Formula (1) is represented by any one of General Formulae (2) to (4) below:



General Formula (2)



General Formula (3)



General Formula (4)

14. The method for producing a polymer sheet according to any one of claims 10 to 13, wherein the polymer layer has a thickness of 1 μm to 20 μm .

15. The method for producing a polymer sheet according to any one

of claims 10 to 14, wherein the polymer contained in the aqueous polymer dispersion liquid has a core-shell structure in which each core portion is covered with a shell portion,

wherein the core portion contains the polymer containing the repeating unit represented by General Formula (1) in an amount of 70% by mass or more and a repeating unit having at least one selected from a carboxyl group, a hydroxyl group and a (meth)acrylamide group in an amount of 0.01% by mass to 30% by mass, and

wherein the shell portion contains the polymer containing the repeating unit represented by General Formula (1) in an amount of 70% by mass or more and the repeating unit having at least one selected from a carboxyl group, a hydroxyl group and a (meth)acrylamide group in an amount of 0.01% by mass to 30% by mass.

16. The method for producing a polymer sheet according to claim 15, wherein the amount of the repeating unit represented by General Formula (1) contained in the core portion and the shell portion is 80% by mass to 97% by mass.

17. The method for producing a polymer sheet according to any one of claims 10 to 16, wherein the support contains at least one selected from the group consisting of polyester resins, polycarbonate resins, polystyrene resins, acrylic resins and polyimide resins.

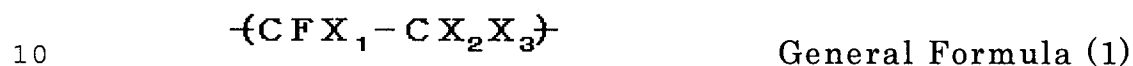
18. The method for producing a polymer sheet according to any one of claims 10 to 17, further comprising heating, at a temperature of 200°C or higher for 5 seconds or longer, the polymer layer which has been formed by applying the aqueous polymer dispersion liquid onto

the support.

19. The method for producing a polymer sheet according to any one of claims 15 to 18, wherein a mass ratio of the shell portion to the core portion is 0.1 to 0.4.

5 20. An aqueous polymer dispersion liquid comprising:
a polymer containing a repeating unit represented by General Formula (1) below,

wherein the amount of the repeating unit represented by General Formula (1) contained in the polymer is 70% by mass or more,



where X_1 , X_2 and X_3 each represent any one of a hydrogen atom, a fluorine atom, a chlorine atom and a perfluoroalkyl group having 1 to 3 carbon atoms.

FIG. 1

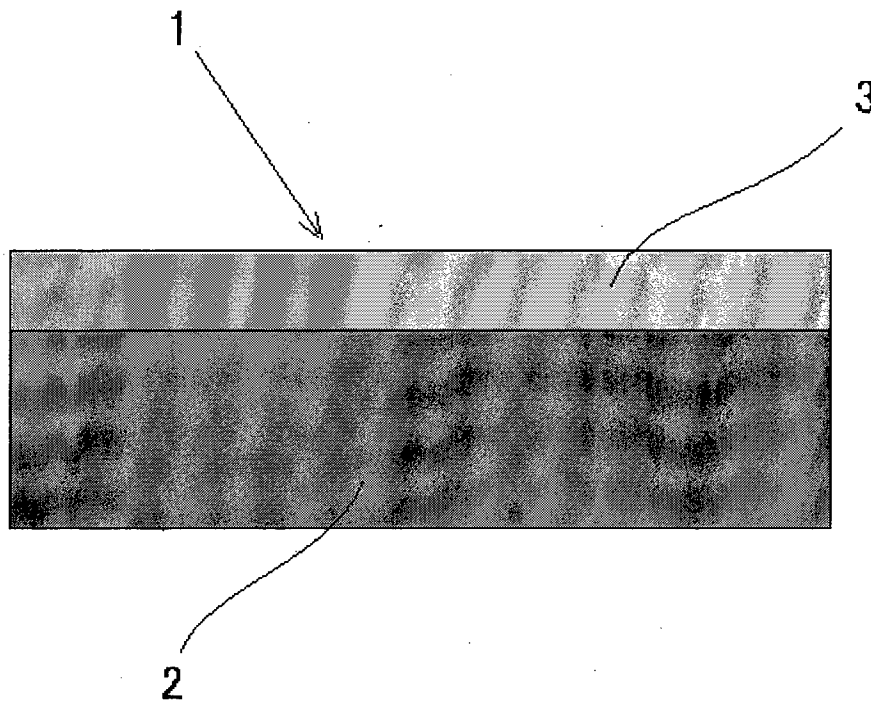
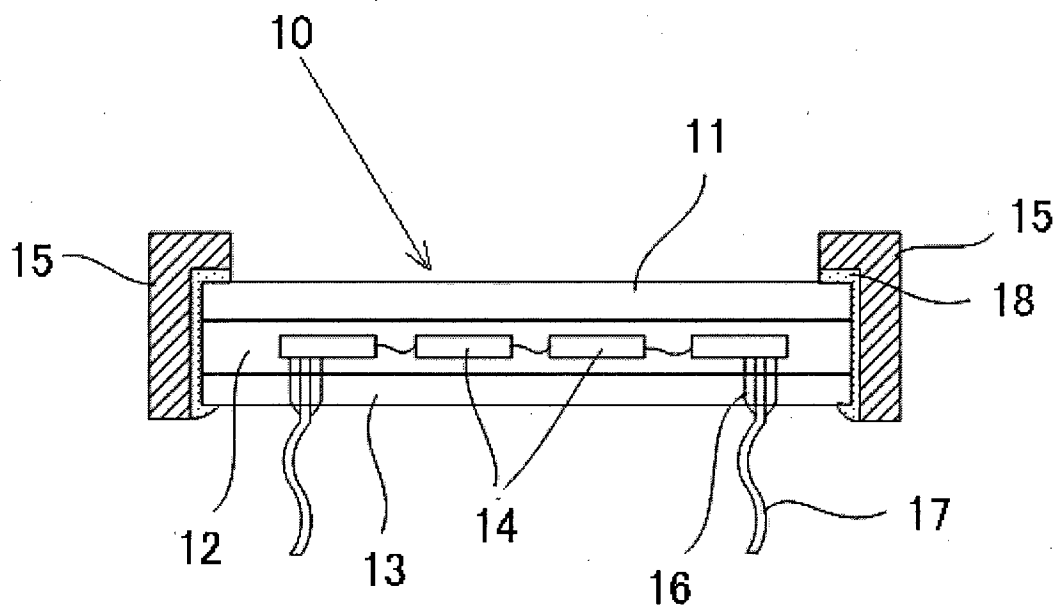


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2011/054219

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D71/36 B32B7/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	EP 2 161 127 A1 (NITTO DENKO CORP [JP]) 10 March 2010 (2010-03-10) paragraphs [0023], [0030]; claim 4 -----	1,4,8,9, 20
X	US 2009/220764 A1 (HATFIELD MARTIN G [US] ET AL) 3 September 2009 (2009-09-03) paragraphs [0021], [0032] -----	1
A	EP 1 995 053 A1 (DAICEL CHEM [JP]) 26 November 2008 (2008-11-26) paragraphs [0157], [0338]; claim 17 -----	1-20
X	EP 1 939 252 A1 (ASAHI GLASS CO LTD [JP]) 2 July 2008 (2008-07-02) see title of publication -----	20



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

17 June 2011

Date of mailing of the international search report

04/07/2011

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/JP2011/054219

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